

REPORT DOCUMENTATION PAGEForm Approved
OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 4/28/2002	3. REPORT TYPE AND DATES COVERED Peer Reviewed Reprint
4. TITLE AND SUBTITLE Conjugated Polyelectrolytes: Synthesis and Applications		5. FUNDING NUMBERS DAAD19-00-1-0002	
6. AUTHOR(S) Mauricio R. Pinto and Kirk S. Schanze			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Florida, Dept. of Chemistry, PO Box 117200, Gainesville, FL 32611		8. PERFORMING ORGANIZATION REPORT NUMBER UF-NIF-10	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER 40422 - 55 - m S	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.			
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE	
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14. SUBJECT TERMS luorescent sensors, conjugated polyelectrolytes		15. NUMBER OF PAGES 17	
		16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. Z39-18
298-102

20040317 067

Conjugated Polyelectrolytes: Synthesis and Applications

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revised 28 April 2002

Abstract: Conjugated polyelectrolytes are conjugated polymers that feature ionic side groups which render the materials soluble in water and other polar solvents. In this review we summarize recent work which has been carried out to synthesize a variety of new conjugated polyelectrolyte structures, including those with poly(paraphenylene), poly(phenylene vinylene) and poly(phenylene ethynylene) backbone structures. Work that has examined the optical, photophysical and solution properties of these materials is also reviewed. Finally, a brief survey of novel applications of conjugated polyelectrolytes to the fabrication of optoelectronic devices and fluorescent sensors is provided.

Key words: conjugation, polyelectrolytes, polymers, polyanions, polycations, water-soluble polymers, fluorescence

1 Introduction

Conjugated polyelectrolytes (CPEs) have received considerable interest recently due to their unique properties and the promise that they may be technologically useful.^{1–10} CPEs possess an intrinsic tendency to organize into supramolecular architectures in solution and in the solid state owing to electrostatic and hydrophobic interactions.^{9,10} In addition, the materials feature distinctive optical and electronic properties such as strong absorption in the visible region,^{6,8,11} strong fluorescence and conductivity in the doped state.^{12,13} The unique combination of optical, electronic and materials properties exhibited by CPEs makes them versatile materials that may serve as the basis for a new generation of optical, electronic and optoelectronic devices.¹⁴

Polymer chemists have long sought to prepare soluble conjugated polymers (CPs) so that solution polymerization, processing and characterization could be optimized. In the earliest stages CP synthetic chemistry was limited to the production of low molecular weight and sparingly soluble polymers.^{15–17} Owing to the poor solubility of these CPs, detailed structural and molecular weight information was not available from common techniques such as high-resolution NMR, gel permeation chromatography (GPC) or light scattering. The addition of solubilizing side chains onto the conjugated backbone proved very effective in improving the solubility and processibility of CPs.^{18–20} This breakthrough triggered a massive research

effort focused on the synthesis, physicochemical properties and application of structurally diverse CPs.^{21–24}

The production of defect free polymers is one of the major challenges in CP synthesis. As a result of the electronic delocalization along the polymer chain, the electronic, optical and photophysical properties of a CP can be influenced profoundly by just a few defects that are produced as a result of undesired side-reactions that occur during polymerization. For example, in a fluorescent CP excitation energy can be trapped by defect sites bringing about efficient non-radiative excited state decay leading to a material that has a comparatively low fluorescence quantum efficiency.^{25–27}

The advent of new synthetic methodologies based on carbon–carbon bond forming reactions promoted by organometallic catalysts allows the synthesis of relatively defect-free CPs under very mild reaction conditions.^{22–24} Since these metal-catalyzed polymerization reactions can be accomplished in solution, high molecular weight CPs can be obtained. The most prominent techniques currently in use for synthesis of CPs include: poly(paraphenylene)s (PPPs) by Suzuki, Stille and Yamamoto coupling reactions;²⁸ poly(phenylene vinylene)s (PPVs) by the Wittig–Horner and Heck reactions, or the Gilch and Wessling routes;²⁹ and poly(phenylene ethynylene)s (PPEs) by Sonogashira coupling and alkyne metathesis reactions.^{30,31} The various palladium-catalyzed coupling methods (i.e. Suzuki, Stille, Heck and Sonogashira) have gained considerable popularity owing to mild reaction conditions, wide functional group tolerance, and versatility of the solvent used for the polymerization.

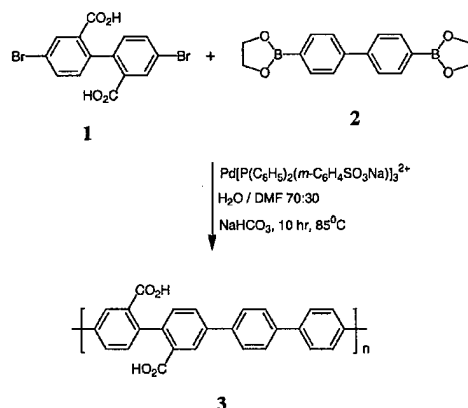
Given the wide range of C–C bond forming reactions that are now available for the synthesis of soluble, high-molecular weight CPs, it is not surprising that these methods are now also being applied to the synthesis of CPs featuring ionic side groups which render the materials soluble in water and other polar protic and aprotic solvents.^{22,24} These reactions are especially useful for the preparation of undoped, mid- and wide-bandgap CPEs. The reports of the synthesis of a water soluble PPV by Shi and Wudl¹¹ and a water soluble PPP by Wallow and Novak³² were the most important initial contributions to this area. In the decade since these early reports appeared, several synthetic methods have been developed, leading to many new CPE structures. Most of the CPEs that have been prepared contain PPP, PPV or PPE backbones decorated with ionic functional groups such as sulphonate (SO_3^-), carboxylate (CO_2^-), phosphonate (PO_3^{2-}) and ammonium (NR_3^+). In

general, these CPEs are strongly fluorescent in solution and in the solid state.

This review article surveys some of the synthetic methods that have been developed for the preparation of CPEs. In addition, we consider some of the physical properties of these new materials, with emphasis placed on thin film formation, optical absorption and fluorescence. These properties have been important in the development of CPEs as active materials for chemo- and bio-sensors. Note that this article is not intended to be a comprehensive survey of all CPEs that have been synthesized. Rather the article is focused on CPEs that have been prepared by solution polycondensation reactions. Importantly, the review does not include work in the area of doped (and undoped) polymers that are prepared by chemical or electrochemical redox polymerization methods.^{12,13}

2 Synthesis

2.1 Water-Soluble Poly(paraphenylene)s



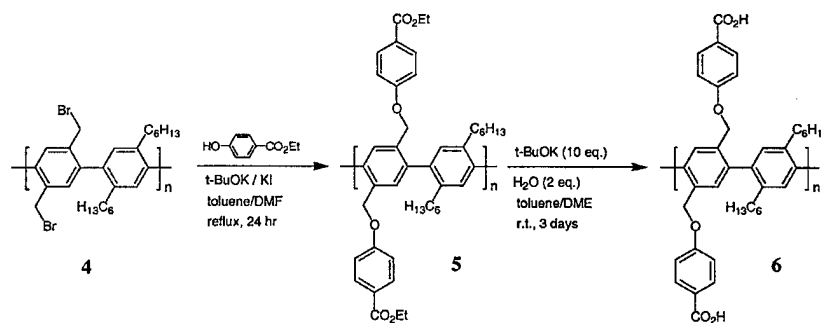
Scheme 1

The first synthesis of a PPP-type CPE was reported by Novak.³² Thus, polymer **3** was synthesized by means of a Suzuki coupling reaction between biphenyl co-monomers **1** and **2** in aqueous solution catalyzed by $\text{Pd}[\text{P}(\text{Ph})_2(m\text{-C}_6\text{H}_4\text{SO}_3\text{Na})_3]_3^{2+}$ (Scheme 1). Although monomer **2** is in-

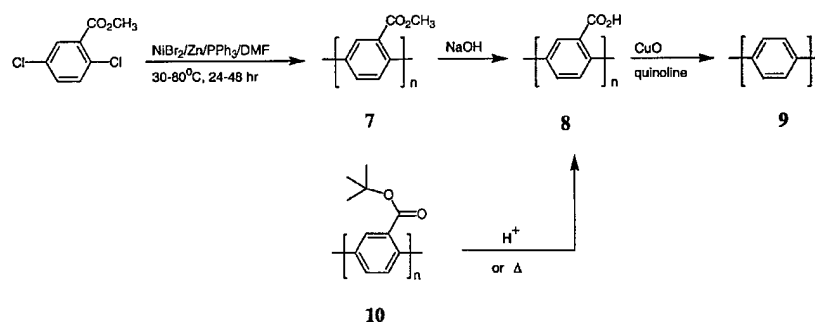
soluble in water, the boronic esters undergo rapid hydrolysis in situ to afford the soluble bis-boronic acid. Dibromide **1** was selected based on model studies of palladium catalyzed coupling reactions between isomers of bromobenzoic acid and tolylboronic acid. Steric hindrance in *o*-bromobenzoic acid hinders the reaction, while *m*-bromobenzoic acid reacts in a quantitative yield.³² Thus, the *meta*-linked carboxyl groups of **1** were not expected to impede the polymerization. Carboxylic acid substituted PPP **3** was isolated from the aqueous medium by precipitation induced by acidification. The acid form of the polymer is insoluble in water and organic solvents, but it is soluble in basic aqueous solution. An apparent molecular weight of 50 kD was determined by polyacrylamide gel electrophoresis analysis using ssDNA as a standard.

A noteworthy feature of PPPs is their relatively high thermal and chemical stability.³³ Because of this intrinsic stability reactions can be carried out on the preformed polymers without leading to degradation of the main chain. Thus, it is possible to change the solubility of a preformed PPP by carrying out reactions on the polymer substituents. Rau and Rehahn³⁴ developed a hydrophobic polymer precursor approach to synthesize a water soluble PPP from precursor **4** that contains reactive alkyl bromide side groups (Scheme 2). A hydrophobic polymer precursor bearing carboxy esters was obtained by Williamson etherification of **4** with ethyl *p*-hydroxybenzoate. The substitution reaction was nearly quantitative, and the resulting polymer was soluble in chloroform, toluene and *o*-dichlorobenzene. An absolute molecular weight of 17 kD was determined by membrane osmometry in *o*-dichlorobenzene. Basic hydrolysis of the ester groups was effected under homogeneous conditions, and the polyelectrolyte isolated by acidification of the reaction medium. The acid form of **6** exhibited solubility in polar organic solvents, such as DMF, DMSO and DMAc.

Kaeriyama and co-workers³⁵ developed a synthetic method to high molecular weight unsubstituted PPP via decarboxylation of a CPE precursor. The initial step was the Ni(0)-promoted homocoupling of methyl 2,5-dichlorobenzoate, which afforded the hydrophobic PPP chain bearing carboxy methyl ester side groups **7** (Scheme 3). This polymer was soluble in chloroform, and consequent-



Scheme 2



Scheme 3

ly a M_n of 6–19 kD was determined by GPC. Subsequent hydrolysis of the ester groups by 10% sodium hydroxide in methanol afforded polyelectrolyte 8, which was soluble in aqueous sodium hydroxide, pyridine and quinoline. Polyelectrolyte 8 was converted to unsubstituted PPP 9 by CuO catalyzed decarboxylation in quinoline. A small improvement of this synthetic approach to PPP 9 was reported by Ueda and Yoneda,³⁶ wherein polyelectrolyte 8 was obtained by acid-catalyzed cleavage of the *tert*-butyl ester groups of 10. According to TGA and FTIR analysis these authors were also able to obtain 8 by thermally induced cleavage of the *tert*-butyl esters. Ueda and Yoneda did not compare the advantages and disadvantages of the two routes to 8.

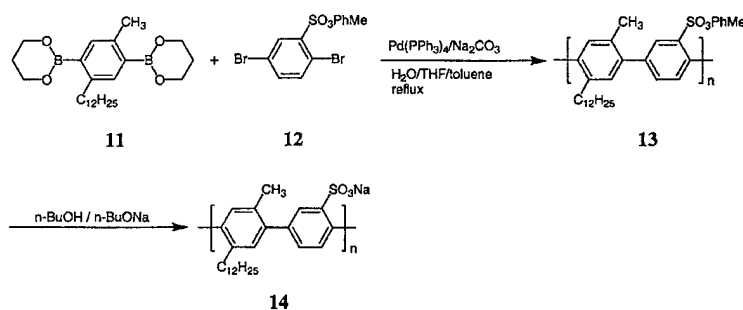
The synthesis of the first sulfonated PPP 14, was reported by Wegner and co-workers.³⁷ The Suzuki coupling of diboronic ester 11 with dibromoaromatic monomer 12 furnished PPP 13 in 95% yield (Scheme 4). An absolute molecular weight of 36 kD was determined by membrane osmometry in toluene. Saponification of 13 in $\text{BuOH}-\text{BuONa}$ afforded CPE 14. Surprisingly, 14 was not soluble in basic aqueous solution, but it was soluble in DMSO. In a subsequent report from the same research group,³⁸ this synthetic approach was extended to produce other isomeric structures. The results of this work provided insight into the unusual solubility behavior of these polymers.

Another approach to sulfonate-substituted PPPs was reported by Child and Reynolds.³⁹ Sulfonate monomer 15 was obtained in three steps starting from 1,4-dimethoxybenzene (Scheme 5). Suzuki co-polymerization of 15

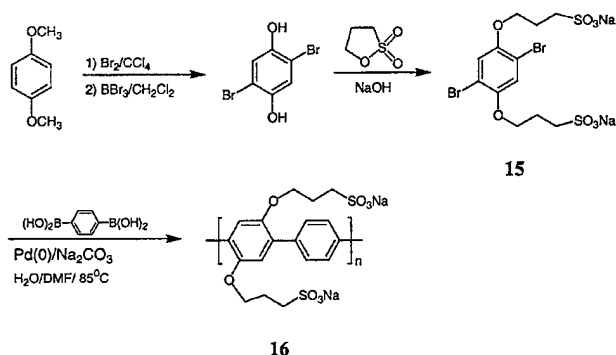
with 1,4-benzene diboronic acid furnished 16 in 64% yield. Although no molecular weight was reported, an aqueous solution of the polymer could be purified by dialysis against water with a 3.5 kD cutoff membrane, suggesting a $M_w > 5$ kD.

Several years later, Reynolds and co-workers¹ extended their work to prepare sulfonated PPP 18 (Scheme 6). This polymer was prepared by the same approach used to prepare 16 by replacing 1,4-benzene diboronic acid with 4,4'-biphenyl diboronic acid ester 17. Polymer 18 was obtained by Suzuki coupling of 15 and 17 catalyzed by $\text{Pd}(\text{PPh}_3)_4/\text{m-SO}_3\text{Na}$ in $\text{H}_2\text{O}-\text{DMF}$ (70:30) in 50% yield.

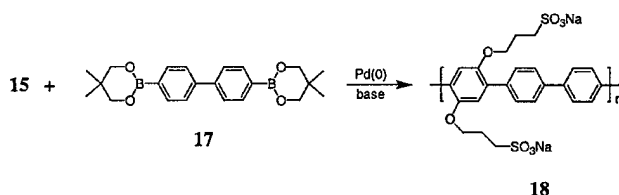
The first cationic CPE was reported by Baullauff and Rehahn.⁴⁰ In order to study the correlation between structure and solution behavior of CPEs, these authors synthesized different cationic PPP-type structures via chemical transformation of a preformed hydrophobic PPP featuring reactive halogenated side chains (Scheme 7). Homopolymer 20 and co-polymer 23 precursors were obtained by an elegant synthetic route, in which monomers having phenoxy-substituted alkyl groups were polymerized by Suzuki coupling. The phenoxy bonds of the resulting PPPs 19 and 22 were cleaved by trimethylsilyl iodide producing reactive primary alkyl iodide groups. Subsequent heating with triethylamine or pyridine furnished the corresponding homo- (21a–b) and co-polymers (24a–b) featuring cationic ammonium groups. The quaternization reaction was nearly quantitative as confirmed by ^1H NMR, while polymer molecular weight was estimated by



Scheme 4



Scheme 5

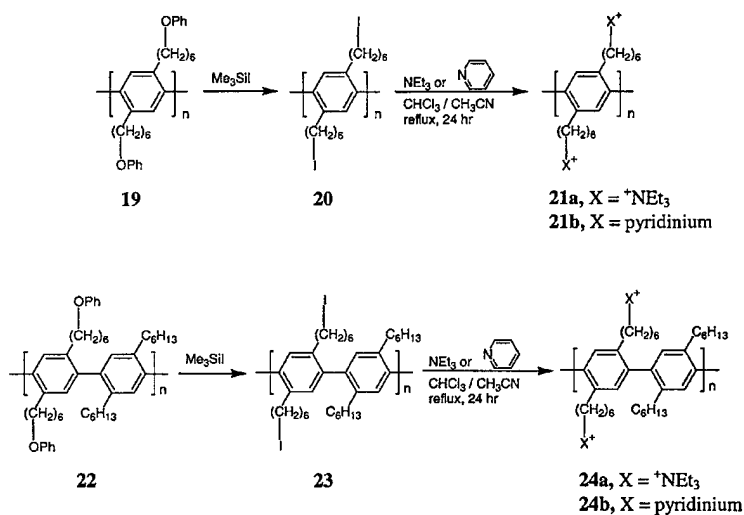


Scheme 6

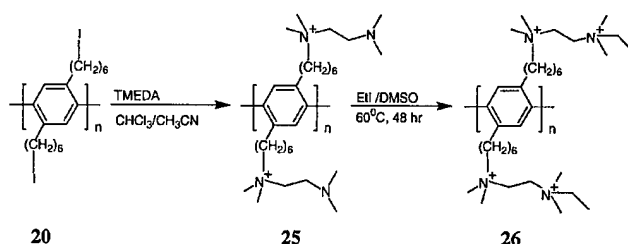
membrane osmometry carried out on hydrophobic precursors. All of the cationic CPEs were soluble in acetonitrile and dimethylacetamide, and homopolymer **21a** was soluble in water. Two years later, Wittemann and Rehahn⁴¹ reported the synthesis of a highly charged cationic PPP using Baullauff and Rehahn's method. Thus, polymer **26** in which each repeating unit carries a 4⁺ charge was obtained in two steps (Scheme 8). First, the hydrophobic homopolymer **20** was reacted with a large excess of tetramethylethylenediamine (TMEDA) to produce **25**, which was further reacted with an excess of iodoethane in DMSO to produce **26**. This last step required a long reaction time in order to attain complete conversion. Cationic

CPEs **25** and **26** were soluble in water and in polar organic solvents.

Another approach to the synthesis of cationic PPP-type CPEs was introduced by Reynolds and co-workers (Scheme 9).² This method involves the application of a Suzuki reaction to polymerize monomer **27** with 1,4-benzene diboronic acid co-monomer. Neutral polymer **28** contains alkoxy side-chains that are substituted with tertiary amine groups, imparting **28** with solubility in CHCl_3 and THF. Consequently, the polymer's structure could be confirmed by NMR spectroscopy, and its molecular weight could be determined by GPC using organic mobile phases. The polymerization yield, molecular weight and



Scheme 7



Scheme 8

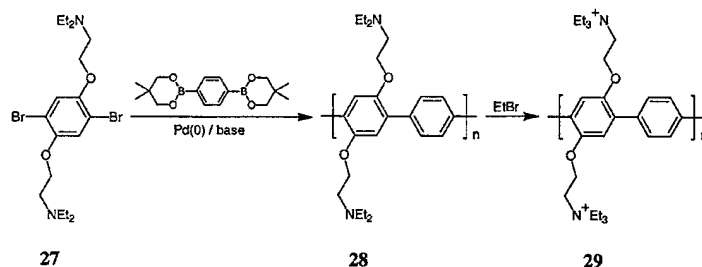
polydispersity of **28** was optimized by systematic variation of the reaction conditions, solvent medium and the catalyst. The $\text{PdCl}_2(\text{dppf})$ catalyst in $\text{THF-H}_2\text{O}$ and NaHCO_3 was demonstrated to be more efficient than $\text{Pd}(\text{AcO})_2\text{-Na}_2\text{CO}_3$ in aqueous THF, DMF or acetone. Under optimum polymerization conditions **28** was obtained with a molecular weight M_n of 19 kD and a polydispersity index of 1.2. After characterization and purification, precursor **28** was converted to the cationic PPP-type CPE **29** by alkylation of the tertiary amine groups with bromoethane under mild conditions. The cationic polymer was freely soluble in water.

Lai, Huang and co-workers⁴² reported the synthesis of a fluorene based cationic CPE by applying the neutral polymer precursor approach developed by Reynolds and co-

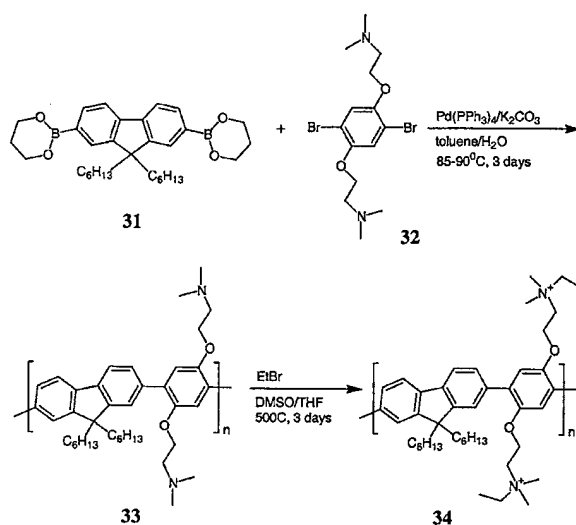
workers. Neutral polymer **33** was obtained in a 70% yield by Suzuki coupling of **31** and **32** in toluene (Scheme 10). This polymer was soluble in CHCl_3 , THF, toluene and aqueous acid, but insoluble in DMSO, methanol and water. A molecular weight of 47 kD was determined by GPC in THF solvent. Alkylation of **33** with bromoethane afforded **34** with a maximum quaternization yield of 80%. Cationic CPE **34** was soluble in DMSO, methanol and water, and insoluble in CHCl_3 and THF.

2.2 Water-Soluble Poly(phenylene vinylene)s

Shi and Wudl¹¹ reported the synthesis of the PPV-type polyelectrolyte **38** by using the Wessling route (Scheme 11). Monomer **35** was obtained from a seven

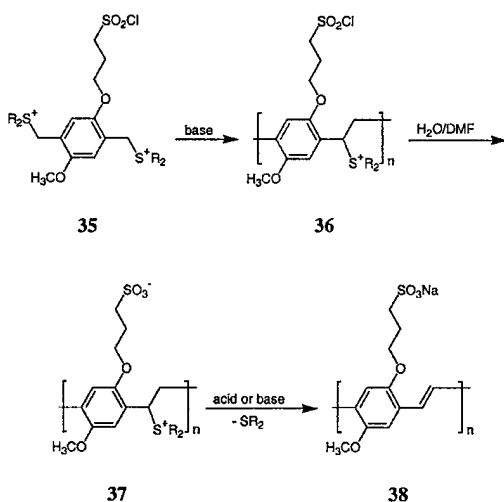


Scheme 9



Scheme 10

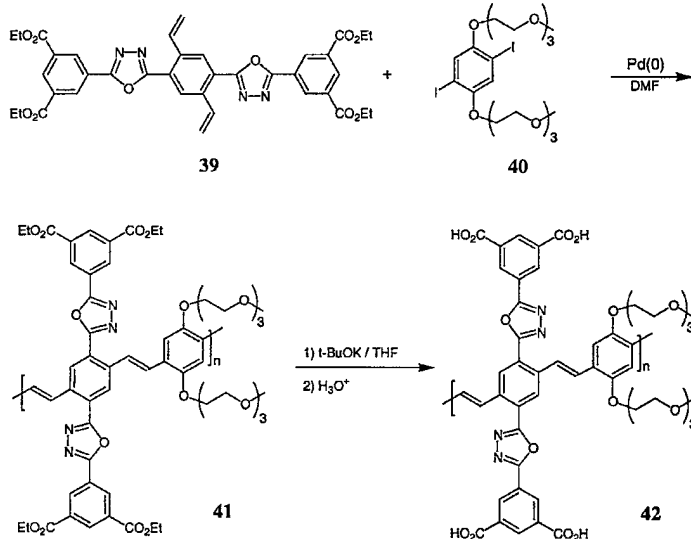
step synthetic sequence in a 16% overall yield. This compound was polymerized under base catalysis to afford the sulfonium polyelectrolyte precursor **36**. The success of this polymerization depended on the purity of monomer **35**. Careful purification of the monomer and optimization of the polymerization conditions were accomplished in order to produce high molecular weight **36**, which was further hydrolyzed in DMF–water under reflux to afford zwitterion **37** after dialysis against water. Sulfonated PPV-type CPE **38** was obtained by acid-catalyzed elimination of precursor **37** in DMF–water solution under very mild conditions. A molecular weight of 1.12×10^6 kD and polydispersity of 16 was determined by aqueous GPC, relative to pullan standards (pullan is an anionic polysaccharide).



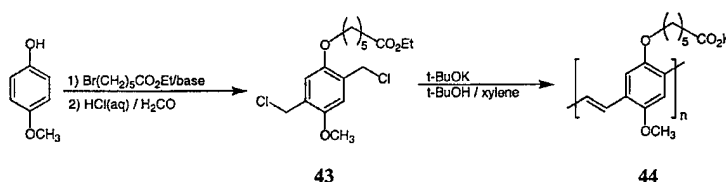
Scheme 11

Peng and co-workers⁴³ designed a PPV-type CPE bearing cross-conjugated side chains with carboxylate groups **42** (Scheme 12). This polymer was designed with the objective of producing a nanoporous polymer network with controllable uniform pore sizes by means of layer-by-layer self-assembly. The carboxylate groups provided the polymer with water solubility and interchain hydrogen bonds in the solid state, acting as 'anchors' during deposition. Polymer **42** was synthesized by base hydrolysis of the carboxy ethyl ester groups in the neutral polymer precursor **41**, which was obtained by a Heck reaction between **39** and **40** catalyzed by $\text{Pd}(\text{OAc})_2\text{-P}(o\text{-Tol})_3$ in DMF. Monomer **39** was obtained from a four step synthetic route in a 12% overall yield. Polymer **41** was soluble in THF, CH_2Cl_2 , but insoluble in DMSO, water and aqueous bases. A molecular weight of 91 kD and polydispersity of 3.2 was determined by GPC analysis. On the other hand, CPE **42** exhibited an opposite solubility trend, being soluble in DMSO and dilute aqueous bases, but insoluble in CHCl_3 and sparingly soluble in THF.

Another water-soluble PPV-type CPE was synthesized by Fujii and co-workers^{44,45} by using a straightforward synthetic approach. Polymer **44** was obtained by direct polymerization of monomer **43** by means of the Gilch route (Scheme 13). CPE **44** was isolated from the reaction medium by acidification. The polymer was soluble in acetone, ethanol, THF, and aqueous NaOH. An interesting feature of this synthetic procedure is that because base-catalyzed alcoholysis of the ethyl ester groups occurs during polymerization, the polyelectrolyte is synthesized directly from a hydrophobic monomer. The synthesis of monomer **43** involved Williamson etherification of 4-methoxyphenol by ethyl 6-bromohexanoate, followed by chloromethylation with concentrated HCl and formaldehyde.



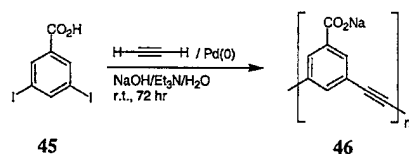
Scheme 12



Scheme 13

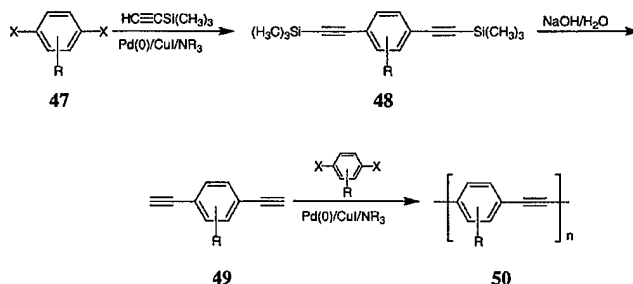
2.3 Water-soluble poly(phenylene ethynylene)s

The first PPE-type CPE was reported by Li and co-workers.^{46,47} This group prepared meta-linked carboxylated PPE **46** in a one-pot synthesis via co-polymerization of acetylene with 3,5-diodobenzoic acid **45** (Scheme 14). The reaction was carried out in aqueous solution, using a water-soluble Pd-phosphine catalyst and CuI–NaOH–Et₃N. A *M_w* of 66 kD was determined by agarose gel electrophoresis analysis with *ds*DNA as standard.



Scheme 14

Poly(phenylene ethynylene)s **50** are typically prepared by means of a Sonogashira co-polymerization of a dihalo-substituted aromatic compound **47** and a diethynyl-substituted aromatic compound **49** (Scheme 15).³⁰ PPEs can also be obtained from metathesis of diethynyl-substituted aromatic monomers;^{30,48} however, this approach has limited functional group tolerance, and has not been applied to synthesis of polymers that contain heteroatom substituents. Diethynyl-substituted monomers are prepared by Sonogashira coupling of trimethylsilylacetylene and dihalo-substituted aromatic compounds, followed by deprotection of the TMS groups.^{49,50} Polymerization is catalyzed by a Pd(0) complex such as Pd(PPh₃)₄, which is either used directly or produced in situ by activation of a Pd(II) species, such as Pd(PPh₃)₂Cl₂.^{49,50} A detailed mechanistic explanation and all the variables of this coupling reaction is given elsewhere.³⁰ PPEs produced from the Sonogashira polymerization generally produce light yellow to green samples that are strongly fluorescent.

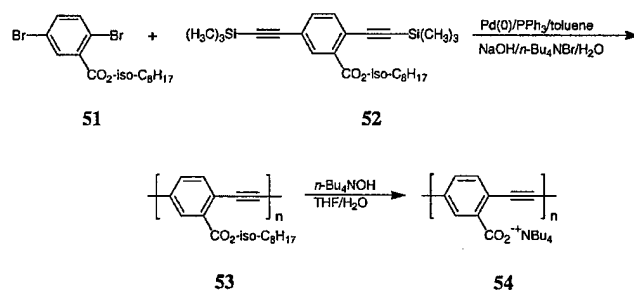


Scheme 15

Another useful technique for PPE synthesis was reported by Häger and Heitz,⁵¹ who proposed that diyne defects could be minimized by maintaining a low stationary state concentration of diethynyl-arene monomer during the polymerization. This is accomplished by slow in situ base-induced cleavage of the trimethylsilylacetylene protecting groups. By using this approach the authors prepared the hydrophobic carboxy ester substituted PPP **53** from a Pd(PPh₃)₄ catalyzed coupling between **51** and **52**, the latter of which underwent in situ desilylation in the basic reaction medium (Scheme 16).⁵¹ The polymer was obtained in a 90% yield and *M_w* of 96 kD with a polydispersity of 8.2 as determined by GPC analysis. The relatively high polydispersity was attributed to the high viscosity and concomitant poor reaction mixing during polymerization. No diyne defects were observed by ¹³C NMR spectroscopy. Hydrolysis of the carboxylate ester groups was accomplished in a THF–water mixture using Bu₄N⁺OH[–]. Complete ester hydrolysis was attained in 24 hours and the resulting CPE **54** exhibited good solubility in water as the tetrabutylammonium and potassium salt. By contrast, the acid form of **54** was insoluble in water.

Swager and co-workers have done extensive work on the synthesis of a variety of PPEs.^{49,50,52–55} With the objective of fabricating solid state pH sensors, this group⁵⁶ synthesized water-soluble, cationic PPE **57** by Sonogashira coupling of **55** and **56** in a DMF–water mixture (Scheme 17). This cationic CPE was soluble in water and DMF and partially soluble in methanol. GPC in DMF solution indicated *M_w* = 67 kD and polydispersity of 1.6. Monomer **55** was obtained by Williamson etherification of 2,5-diiodohydroquinone with 1,3-dibromopropane, followed by reaction with trimethylamine.

In a recent paper, Schanze and co-workers⁸ reported the synthesis of sulfonated PPE **59** which was obtained by Sonogashira coupling of **58** with 1,4-diethynylbenzene in a DMF–water mixture catalyzed by Pd(PPh₃)₄–CuI

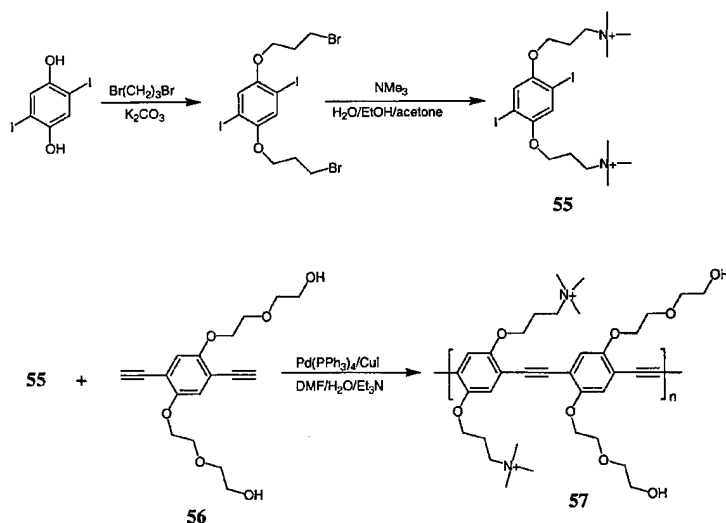


Scheme 16

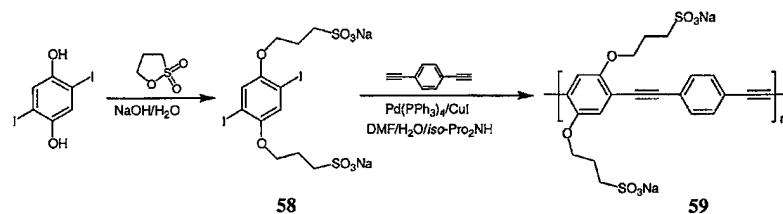
(Scheme 18). The resulting polymer was obtained in a 68% yield, and it was soluble in water and low molecular weight alcohols. A molecular weight of 100 kD was estimated by the polymer's ultrafiltration properties and by iodine end-group analysis. Monomer 58 was obtained from 2,5-diiodohydroquinone in one step in a 70% yield.

In a recent preliminary report, Pinto and Schanze⁵⁷ described the PPE-type CPE 63 (Scheme 19), which features phosphonate groups appended to the polymer backbone. The phosphonate CPE was prepared via a neutral precursor polymer, which was soluble in organic solvents, enabling the material to be characterized by NMR

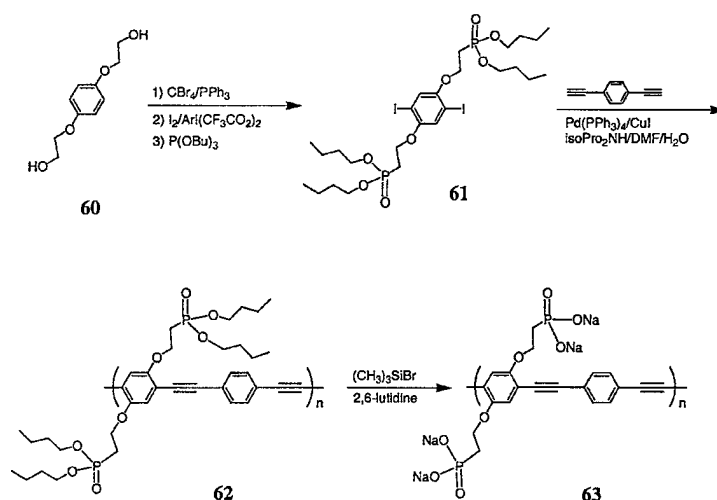
and organic GPC. The required phosphonate substituted monomer 61 was obtained in three steps in a 46% overall yield beginning with diol 60. Sonogashira polymerization of phosphonate monomer 61 and 1,4-diethynylbenzene afforded neutral polymer 62 in a 46% yield. Analysis of the neutral CPE-precursor indicated $M_w = 18.3$ kD and polydispersity of 2.9. CPE 63 was prepared by bromotrimethylsilane-induced cleavage of the *n*-butyl phosphonate ester groups in 62. After neutralization of the reaction mixture with aqueous sodium hydroxide, CPE 63 exhibited good solubility in water.



Scheme 17



Scheme 18



Scheme 19

3 Solution Behavior of Conjugated Polyelectrolytes

The solution properties of polyelectrolytes differ significantly from those of neutral polymers.⁵⁸ Interplay between polymer-solvent and electrostatic interactions and chain flexibility is responsible for the unusual solution properties of polyelectrolytes relative to neutral polymers.⁵⁹ The importance of electrostatic interactions is determined by polyelectrolyte concentration, the degree of ionization of the ionic groups, and by the ionic strength of the medium.⁶⁰ For example, for a flexible polyelectrolyte in a dilute salt-free solution, the reduced viscosity increases with decreasing polyelectrolyte concentration.⁶¹ This is explained by a change of the polymer morphology from random coil to an extended rod-like structure induced by increased electrostatic repulsion between monomeric units with decreasing polymer concentration.⁶² An increase in solution ionic strength, arising from increased polymer or salt concentration, screens the interchain electrostatic repulsions, restoring random coil morphology. Under this condition the polyelectrolyte behaves like a non-ionic polymer, i.e. the reduced viscosity increases linearly with polymer concentration.^{63–65}

Because the conformation of a CPE chain is somewhat restricted by the conjugated structure of the backbone, intra-chain electrostatic interactions are believed to have a minimal effect on chain conformation.^{40,66} Thus, the solution behavior of a CPE is influenced primarily by inter-chain and hydrophobic interactions. Nonetheless, viscosity studies of PPP-type polyelectrolytes conducted in the presence and absence of added salt demonstrate that at least some CPEs behave as semi-flexible polyelectrolytes.^{1,38,40} For instance, Reynolds and co-workers¹ conducted viscosity experiments on sulfonated PPP **16** in dilute aqueous solutions at different ionic strengths. As illustrated in Figure 1, in pure water the reduced viscosity

of **16** increases significantly with decreasing polymer concentration. This effect is attenuated as the ionic strength increases, and in concentrated salt solution the reduced viscosity of the polymer is virtually independent of concentration.

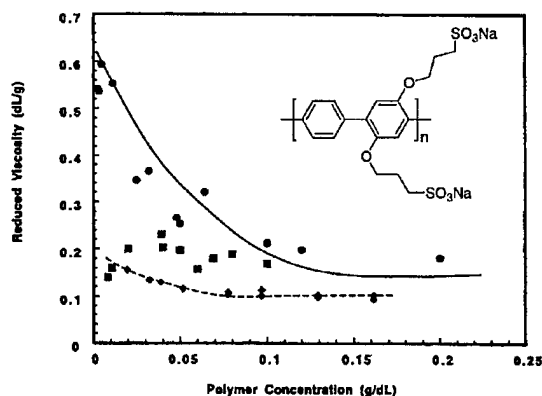


Figure 1 Reduced viscosity as a function of the concentration of PPP-type CPE **16** in different ionic strengths: (●) pure water; (■) aq NaNO₃ (0.001 M); (◆) aq NaNO₃ (0.1 M). The solid and dashed lines are drawn through the data points in salt-free and 0.1 M salt solutions, respectively. Reproduced from reference¹ with permission from the American Chemical Society.

Polymer persistence length provides a relative measure of polymer chain flexibility.⁶⁷ Persistence lengths in the range of 22–28 nm for PPP-type polyelectrolytes and greater than 80 nm for a PPV-type polyelectrolyte have been determined in salt-free aqueous solutions,^{40,68,69} which implies that these polymers adopt rather extended conformations in solution. These polymers can be considered to be more rigid than cellulose derivatives (10–14 nm),⁶⁷ but comparable to DNA (60 nm)⁶⁷ and poly(1,4-

benzamide) (75 nm)⁶⁷ in solution, which are known to be very stiff structures.

An interesting feature of CPEs is that they have a tendency to form lyotropic phases in solution at low to moderate concentrations.^{37,38,70} It is believed that CPE chains assume a cooperative orientational order in solution above the overlap concentration (i.e. $c > c^*$), as a result of the anisotropic shape of the chains and strong π - π interactions. Wegner and co-workers observed birefringence from solutions of a PPP-type CPE at concentrations as low as 2 g/dL.³⁸ Manipulation of the hydrophobic-hydrophilic balance of CPEs allows control of supramolecular structure both in solution and in the solid state. Supramolecular structure can also be influenced by electrostatic interactions between CPEs and amphiphiles. Thünemann and co-workers⁷¹ produced cylindrical aggregates in solution and columnar mesomorphous structures in the solid state by using complexes of a cationic PPP-type polyelectrolyte and a perfluorated amphiphilic anion. This group also demonstrated the formation of different mesophases from complexes of an anionic PPE-type polyelectrolyte by using different amphiphilic cations.⁷¹

Strong hydrophobic association of CPEs is also responsible for polymer aggregation even in very dilute solutions.⁷² This effect has been pointed out as being the major impediment to precise structural characterization of CPEs in aqueous solution by methods such as GPC and light scattering.^{2,34,37,38,42} This situation can be overcome in part by the neutral polymer precursor approach, in which structural information concerning a CPE is obtained by analysis of a polymeric precursor.²

4 Photophysical Properties

The photophysical properties of CPEs dissolved in polar organic or aqueous solutions generally parallel those of their neutral counterparts dissolved in organic solvents. Specifically, the absorption energy (bandgap) of the CPEs varies in the order PPP > PPE > PPV.^{2,8,11} In addition, in most cases the materials are strongly fluorescent.^{2,5,8} The Table collects representative photophysical data for some of the CPEs described in the previous sections. In some cases detailed data is available, such as fluorescence quantum yields and lifetimes, and in other cases only an absorption maximum is reported.

When a CPE exists in solution in a non-aggregated state, the photophysical properties of the material are remarkably similar to those of a neutral analog dissolved in a non-polar organic solvent. For example, Reynolds and co-workers reported that the fluorescence maximum and quantum yield of PPP-type CPE 16 (Scheme 5) in dilute aqueous solution are 410 nm and 0.60, respectively.¹ By comparison this same group finds that a structurally analogous, neutral PPP that is functionalized with alkoxy-

side groups features a fluorescence maximum and quantum yield of 406 nm and 0.70, respectively, in chloroform solution.⁷³ On the other hand, photophysical studies provide very clear evidence that in aqueous solution CPEs have a very strong tendency to aggregate, and this aggregation phenomenon has a substantial influence on the photophysical properties of the polymers. For example, Whitten and co-workers⁵ report that sulfonated PPV 38 (Scheme 11) has a fluorescence maximum of 590 nm and a quantum yield of ca. 0.01. By comparison, the neutral analog MEH-PPV has a fluorescence maximum of 558 nm and a quantum yield of 0.35 in solution.^{74,75} The red-shift and significantly decreased fluorescence quantum yield for CPE 38 in aqueous solution is believed to arise due to inter-chain aggregates which produce excimer-like trap states for the $^1\pi, \pi^*$ exciton.

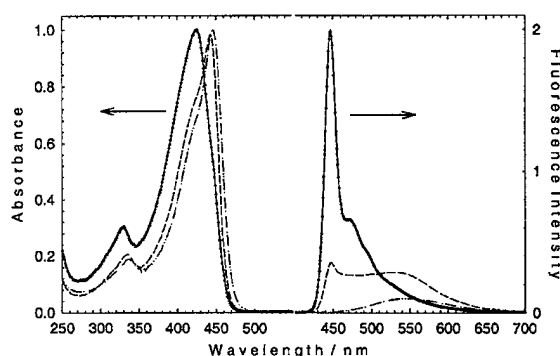
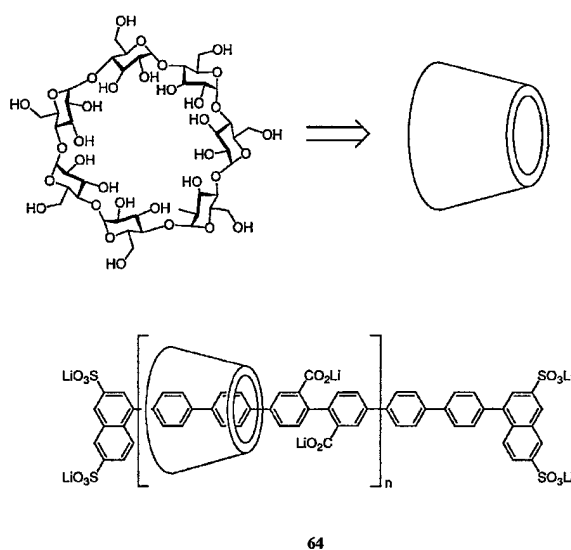


Figure 2 Absorption (left) and fluorescence (right) spectra of PPE-type CPE 59: in MeOH (—◆—), in H₂O-MeOH (1:1) (---), in H₂O (—). Reproduced from reference⁸ with permission from the Royal Society of Chemistry.

In a very recent study, Schanze and co-workers reported the solvent-dependence of the absorption and fluorescence of PPE-type CPE 59 (Scheme 18) which provides very clear evidence for the strong effect that aggregation has upon the photophysics of CPEs.⁸ Figure 2 illustrates the spectra of a dilute solution of 59 in methanol, methanol-water and water. Two features are readily apparent from this data. First, as the volume fraction of water in the solvent increases, the absorption red-shifts and narrows. Second, with increasing water content, the fluorescence red-shifts and broadens significantly, and the fluorescence quantum efficiency decreases. All of these features are consistent with a model in which the CPE exists in a relatively unaggregated state in methanol, but in water rich solvents the polymer aggregates. The red-shift and narrowing of the absorption that accompanies aggregation is attributed to an increase in the structural ordering of the phenylene rings in the PPE backbone. The red-shift and broadening of the fluorescence is attributed to the formation of an excimer-like state arising from inter-chain π - π

stacks. Both of these effects are attributed to the aggregated polymer having a lamellar structure, where the chains are relatively aligned in order to optimize π - π and hydrophobic interactions.⁸

Inclusion complex formation between CPEs and hydrophilic hosts is one method to suppress polymer aggregation. Inclusion complexes can increase the hydrophilicity of a CPE and provide a steric barrier to polymer aggregation. Anderson and co-workers⁷⁶ reported the synthesis of a β -cyclodextrin insulated PPP-type polyelectrolyte. Thus, rotaxane **64** (Scheme 20) was synthesized by polymerization of cyclodextrin inclusion complexes of the monomer in aqueous solution. Terminal bulky groups were installed to prevent release of the β -cyclodextrin units. The photophysical properties of polyrotaxane **64** were compared to those of corresponding non-complexed CPE. The fluorescence of the polyrotaxane was blue-shifted by 20 nm and the fluorescence quantum yield was enhanced slightly. These observations are consistent with the cyclodextrin preventing interchain excimer formation.

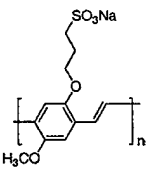
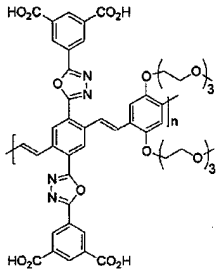
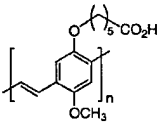
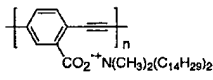
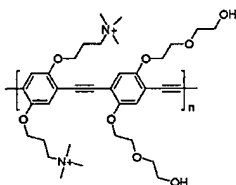
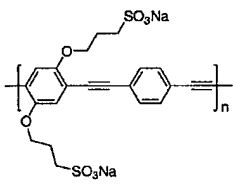
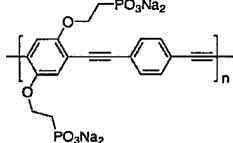


Scheme 20

Table Photophysical Properties of CPEs

Structure	Mol. Weight (Method)	λ_{\max} (nm) Abs. (ϵ_{\max} M ⁻¹ cm ⁻¹)	λ_{\max} (nm) Fluor. (ϕ_F)	Remarks
	5.0×10^4 (GPC and PAGE)	215, 335 in H ₂ O	430 (0.18) in H ₂ O	Ref. ⁷⁶
	$7\text{--}14 \times 10^3$ (GPC of the neutral precursor)	233, 322	-----	Ref. ³⁵
	1.9×10^4 (end group analysis)	244 (11000), 286 (10200), 338 (15200) in H ₂ O	410, 430sh (0.60) in H ₂ O	$\tau_{1/2} = 1.0$ ns in H ₂ O ¹
	$9\text{--}10 \times 10^3$ (GPC of the neutral precursor)	290, 330 (21000 in H ₂ O; 8000 in THF)	408 in H ₂ O	$\tau_{1/2}$ ca. 600 ps Ref. ⁴
	4.7×10^4 (GPC of the neutral polymer precursor)	343 in H ₂ O; 354 in MeOH; 367 in DMSO	409 in H ₂ O; 409 in MeOH; 419 in DMSO (0.86 in MeOH; 0.25 in H ₂ O)	Ref. ⁴²

Table Photophysical Properties of CPEs (continued)

Structure	Mol. Weight (Method)	λ_{\max} (nm) Abs. (ϵ_{\max} , $\text{M}^{-1} \text{cm}^{-1}$)	λ_{\max} (nm) Fluor. (ϕ_F)	Remarks
	$1.0\text{--}5.0 \times 10^5$ (light scattering)	475	590	Ref. ⁵
	9.1×10^4 (GPC of the neutral precursor)	484 in aq NaOH (dilute)	555 and 595sh in DMSO; 593 in aq NaOH (dilute) (0.042)	Ref. ⁴³
	-----	425 in THF; 360, 440 in the solid state	535 in THF; 555 (0.07) in the solid state	Ref. ^{44,45}
	1.0×10^5 (GPC)	277, 296, 315 in CHCl_3 ; 294, 311 in MeOH; 278, 315 in THF	430, 453sh in THF	Ref. ¹⁰
	6.7×10^4 (GPC)	439 in the solid state	471 (0.08) in the solid state	Ref. ⁵⁶
	1.0×10^5 (ultrafiltration and end group analysis)	425 in MeOH; 444 in H_2O	447 (0.78) in MeOH; 548 (0.10) in H_2O	$\tau_{1/2} = 420\text{ps}$ in MeOH ⁸
	5.5×10^4 (GPC of the neutral polymer precursor)	412 in H_2O at pH 11.0 and 444 at pH 7.5	437 (0.05) in H_2O at pH 11.0; 518 (0.03) at pH 7.5	Ref. ⁵⁷

5 Layer-by-Layer Self-Assembled Film Deposition

Most applications of conjugated polymers in electronic, optoelectronic, electrochemical or sensing devices require

the materials to be fabricated in a thin film format. The most common technique for fabricating thin films of neutral CPs is by spin-coating, however some groups have successfully fabricated organized multi-molecular layer films by the Langmuir–Blodgett method.^{77,78} An alterna-

tive method is available for fabricating nano-structured, multilayer thin films of CPEs. This method, which involves layer-by-layer (LBL) deposition of oppositely charged polyelectrolytes, has received considerable attention since its discovery in the early 1990's.^{79,80}

Interestingly, it is possible to control the thickness and morphology of LBL films by varying the deposition solution conditions.⁸¹ Specifically, polyelectrolyte deposition from low ionic strength solutions produces relatively thin and flat films, in which the polymer chains are tightly packed.⁸² Conversely, deposition from high ionic strength solutions produces relatively thicker films with a rough surface topology, presumably due to polymer chain entanglement and interpenetration between layers.⁸² LBL deposition of weak polyelectrolytes is strongly influenced by the pH of the medium, due to the effect of pH on the degree of ionization of the weak polyelectrolyte.^{83,84} The LBL deposition mechanism can be even more complex in the case of conjugated polyelectrolytes, since electrostatic and hydrophobic interactions between polymer chains may influence the polymer's morphology in solution, which in turn will affect the film morphology.

Rubner and co-workers⁸⁵ produced films via LBL deposition of the anionic PPP-type CPEs **16** and different cationic polyelectrolytes. This group showed that layer

thickness could be controlled over the range 5–45 Å by addition of sodium chloride to the polyelectrolyte solutions. The thickness also depended on the type of polycation used in the deposition according to the following trend: PPV precursor < poly(allylamine hydrochloride) < cationic PPP **29** < poly(vinylpyridine) < poly(ethyleneimine). More recently, the same research group evaluated layer interpenetration by using Förster energy transfer from PPP to PPV bilayers that were separated by non-conjugated polyelectrolyte bilayers.³ McBranch and co-workers^{86,87} compared the spectroscopic properties of polyelectrolyte LBL films consisting of two cationic non-conjugated polyelectrolytes, poly(ethyleneimine) (PEI) or dendrimer **65** (Figure 3), with the anionic PPV-type CPE **38**. The absorption of **38** was red-shifted by 30 nm and the fluorescence quantum yield was enhanced when the LBL films contained dendrimer **65** rather than PEI. The fluorescence was further enhanced when non-conjugated polyelectrolyte spacer layers were inserted between layers of **38**.

Pinto and Schanze recently reported the fabrication of LBL films using PPE-type CPE **63** which features phosphonate side groups.⁵⁷ LBL films were deposited using this polymer by two approaches. In the first, multilayer films were deposited consisting of alternate layers of **63** and the polycation poly(dimethyldiallylamine) (PDDA).

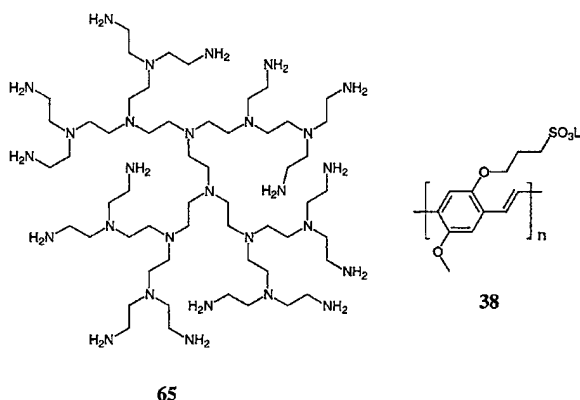


Figure 3

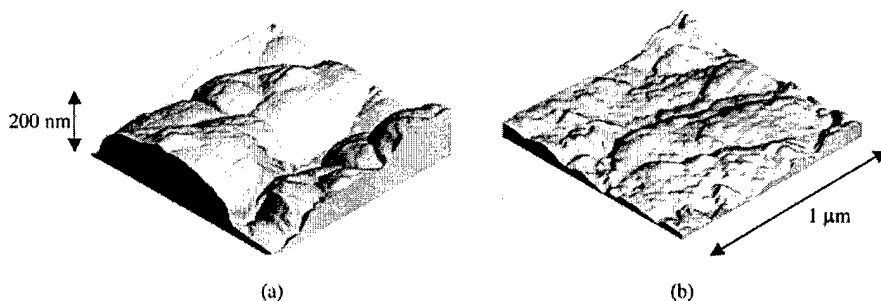


Figure 4 Tapping mode AFM micrographs of LBL films: (a) **63** and poly(dimethyldiallylamine chloride); (b) **63** and Zr(IV). Five bilayers were deposited onto a glass substrate from water–DMSO (50:50) solutions at pH 4.0.

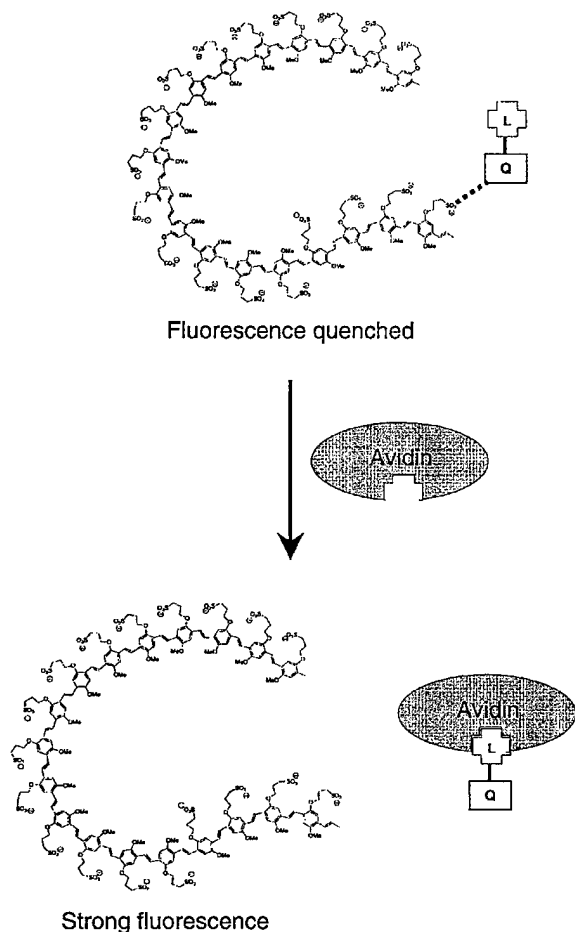
The thickness of these films was strongly dependent on the pH, presumably due to the variation in the degree of ionization of the phosphonate groups, and also due to effects of pH on the degree of aggregation of the polymer in solution. In a second approach to construction of ultrathin films, these authors used Zr(IV) to 'template' the deposition of **63**. Thus, a substrate was 'primed' with Zr(IV) using a published procedure,^{88,89} and then the surface was exposed to an aqueous solution of **63**. Multilayer LBL films were then constructed by alternately depositing Zr(IV) and **63**. The authors found that the thickness of the Zr(IV)-**63** multilayer films was pH dependent, but in general the Zr(IV) 'templated' films were thinner than those fabricated by alternate deposition of PDDA and **63**. Interestingly, examination of the surface of the multilayer films using AFM revealed that the surface morphology of the Zr(IV)-**63** films was relatively smoother compared to that of the PDDA-**63** films (Figure 4). The authors attributed this difference to the formation of 'globular' aggregates between the PDDA and **63** concomitant with film deposition. Evidence for the aggregation was provided by spectroscopic investigation of the films.

6 Applications of Conjugated Polyelectrolytes

One of the most active areas in conjugated polymer chemistry and physics is the development of polymer light emitting diodes (PLEDs). Not too surprisingly, a number of groups have explored the application of CPEs to fabricate PLEDs. In one of the first applications in this area, Rubner and Reynolds⁸⁵ reported the fabrication of PLEDs in which the active material was deposited by the LBL technique using the pair consisting of cationic PPP **29** and anionic PPP **16**. The PLED fabricated using the CPEs displayed blue electroluminescence, and the device operated with modest efficiency. In another report, Yang, Wudl and Reynolds⁹⁰ reported the use of inkjet printing to fabricate pixelated PLEDs, which featured the cationic PPP-type CPE **29** and MEH-PPV as the active materials. In the hybrid device, CPE **29** was applied to the transparent anode by spin-coating, and subsequently the MEH-PPV was applied in a pattern by using an inkjet printer. The resulting device emitted blue light from the areas where only **29** was present, and red-orange in regions where the MEH-PPV was applied by the inkjet printer. Thünemann and Ruppelt⁹¹ recently reported the fabrication of PLEDs that contain complexes of an anionic PPE-type CPE with cationic ammonium amphiphiles as the active material. The devices were fabricated by spin-coating the CPE-surfactant complex onto the indium tin oxide anode from an organic solvent. An aluminum cathode was then deposited to complete the device fabrication. The PPE-containing devices exhibited blue-green electroluminescence with maxima in the 430–520 nm region; the color of the electroluminescence was a function of the amphiphile used in the salt.

Another area of widespread interest that involves the application of conjugated polymers is the construction of conjugated polymer-based photovoltaic (PV) devices. Work in this area was stimulated by the report by Heeger, Wudl and co-workers⁹² that relatively efficient PV devices could be fabricated by blending a conjugated polymer with an electron acceptor such as C₆₀. Although there has been limited work on the fabrication of PV devices that contain one or more CPEs as the active material, it is likely that this area will see increased activity because of the ease by which nano-structured, CPE-based films can be fabricated by the LBL approach. A group at the Air Force Research Laboratory⁹³ recently reported the construction and characterization of PV devices that were fabricated by the LBL deposition approach using an anionic polyelectrolyte precursor to PPV as the light absorber and electron donor and a cationic derivative of C₆₀ as the electron acceptor. The polyelectrolyte precursor was converted to PPV by heating the device under vacuum after LBL film deposition. The PV devices exhibited modest light-to-electrical energy conversion efficiencies, and the photocurrent action spectra confirmed that the PPV functioned as the primary light absorber.

The area which has received the most excitement in the application of CPEs is in the development of highly sensitive fluorescence-based sensors for chemical and biological targets.⁹⁴ Work in this area was stimulated by the initial report by Whitten, McBranch and co-workers⁵ that the fluorescence of the anionic PPV-type CPE **38** is quenched by extremely low concentrations of cationic quenchers such as *N,N'*-dimethylviologen (MV²⁺). This 'amplified quenching' effect is believed to arise due to: (1) ion-pairing between the quencher and the conjugated polymer; and (2) extremely rapid exciton diffusion along the CPE chain to the quencher 'trap-site'. Taking advantage of the amplified quenching effect, this group devised a 'turn-on' fluorescence sensor, which could be tailored to be specific for virtually any biological target by using the 'quencher-tether-ligand' (QTL) approach. The QTL approach involves the use of a cationic quencher (e.g. MV²⁺) covalently linked by a flexible tether to a ligand which is specific for a biological macromolecule such as a protein, nucleic acid or a toxin. The group demonstrated this technology by using the system consisting of CPE **38** and the QTL **B-MV**, which contains the MV quencher unit covalently linked to biotin, which is a ligand that binds strongly to receptor sites in the proteins avidin and streptavidin (Scheme 21).⁵ When **38** is in aqueous solution with a low concentration of **B-MV** (e.g. 100 nM), the polymer's fluorescence is suppressed by the amplified quenching effect. However, addition of very small aliquots of the protein avidin, which binds very strongly to biotin, leads to a significant increase in the fluorescence intensity of **38**. This 'turn on' of the fluorescence is believed to occur because the **B-MV** binds more strongly to the avidin than the CPE, thereby releasing the MV quencher from the CPE chain (Scheme 21). Subsequent to this initial discovery, the group has extended the CPE-



Scheme 21

based sensor system to detect a variety of targets, including the cholera toxin.⁹⁵ The group has also discovered that the sensitivity of the system is improved markedly when the PPV-type CPE **38** is replaced by the PPE-type anionic polymer **59**. The sensitivity enhancement is believed to arise primarily because the fluorescence quantum efficiency of **59** is 15 times higher than that of **38**.

In very recent work, DiCesare and co-workers reported the development of a CPE-based sensor for carbohydrates.⁹⁶ This turn-on sensor system is based on the anionic PPE-type CPE **59** and the boronic ester-derivatized

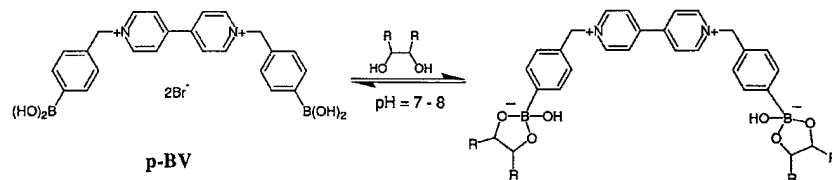
quencher **p-BV** (Scheme 22). The basis for the operation of this sensor is that the cationic charge on **p-BV** is neutralized when the boronic acids form ester complexes with the diol unit in a carbohydrate, Scheme 22. Neutralization of the cationic charge destroys the ion-pair interaction between **p-BV** and CPE **59**, which in turn leads to a substantial increase of the polymer's fluorescence. This sensor system is able to detect fructose at concentration levels $< 50 \mu\text{M}$ in aqueous solution, and its sensitivity is believed to be an improvement by over a factor of 10 of previous fluorescence based sugar sensors.

7 Outlook and Conclusion

It is evident from the scope of this review that there is significant research activity in the area of conjugated polyelectrolytes. A number of new synthetic methods have been developed, and a variety of new polymer structures have been synthesized that feature tunable optical and electronic properties. One of the more interesting and unique features of many CPEs is their solubility in water. This feature makes it possible to process the materials in an environment-friendly solvent. This is a clear advantage over neutral conjugated polymers, which must be processed in organic solvents. In addition, the water solubility of many CPEs makes it possible to use them in solvent environments that are compatible with biological systems, allowing the development of new sensors for biological analytes.

Although a great deal of progress has already been made towards the synthesis and understanding of the solution properties of CPEs, much is yet to be done in this area. A significant problem that needs to be solved is the development of one or more routine methods for determination of the molecular weights of CPEs. Because of their limited solubility in typical organic solvent systems, application of routine GPC methods is often infeasible. In addition, because of the propensity of CPEs to aggregate in solution, application of light scattering to the determination of molecular weight and polydispersity is complicated.

Even though the tendency of CPEs to aggregate in solution presents difficulties with respect to their structural characterization, there may be opportunities that arise from this property. For example, studies of the amplified quenching effect suggest that exciton delocalization between aggregated chains can lead to additional sensitivity in the quenching process.⁸ The formation of well-defined, supramolecular CPE aggregate structures may allow con-



Scheme 22

trol of optical properties such as fluorescence or electroluminescence polarization. Studies directed at understanding the structure–property relationships, which control the solution and aggregation properties of CPEs may ultimately provide sufficient insight to allow one to control the solution properties and aggregate structures through structural design and solution conditions (i.e. solvent polarity and salt and amphiphile concentration).

The area of CPE synthesis and characterization is relatively new, yet already a number of technologically useful applications have emerged. Indeed, at least one new start-up company has been founded which seeks to capitalize on the sensor properties of CPEs to develop a range of new optical sensors for biological analytes.⁹⁷ There is also significant promise that CPEs will serve as a platform for the development of sensors for bio-warfare agents, including anthrax. Moreover, there is the distinct possibility that CPEs will find application in opto-electronic and electronic devices, such as PLEDs, polymer based photovoltaics, electrochromics and polymer lasers.

It is clear that the future is bright for the field of conjugated polyelectrolytes. Much has already been learned due to the excellent work of the many groups that have contributed to the area in the last decade. Only time will tell how this new and unique family of organic-based materials will be applied to improve man's standard of living.

Acknowledgement

The authors acknowledge the Army Research Office and the Defense Advanced Research Projects Agency (DAAD19-00-1-0002) for support.

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